



TITLE:

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CITATION:

Seto, Makoto ...[et al]. Synchrotron-Radiation-Based Mössbauer Spectroscopy. Physical Review Letters 2009, 102(21): 217602.

ISSUE DATE:

2009-05

URL:

<http://hdl.handle.net/2433/85356>

RIGHT:

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## Synchrotron-Radiation-Based Mössbauer Spectroscopy

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(Received 23 August 2008; published 27 May 2009)

We have developed a new method that yields Mössbauer absorption spectra using synchrotron radiation (SR); this method is applicable for almost all Mössbauer nuclides including those that cannot be measured by previous methods using radioisotope (RI) sources. The Mössbauer spectrum of the 68.752 keV excited state of <sup>73</sup>Ge, which cannot be measured using a RI source, was measured using SR. Our results show that this method can be used to perform advanced Mössbauer spectroscopy measurements owing to the excellent features of SR.

DOI: [10.1103/PhysRevLett.102.217602](https://doi.org/10.1103/PhysRevLett.102.217602)

PACS numbers: 76.80.+y, 78.70.Ck, 82.80.Ej, 87.64.kx

Mössbauer spectroscopy [1] is a powerful and well-established method employed for conducting research in various fields such as physical, chemical, biological, earth, and fundamental physical sciences. Mössbauer spectroscopy provides element-specific information on surrounding electronic states and magnetism, which is required in modern materials science and in complex systems such as biological substances. Mössbauer effects can be observed for approximately 100 nuclear transitions of nearly 50 elements. However, we think that, except for some elements such as <sup>57</sup>Fe, <sup>119</sup>Sn, and <sup>151</sup>Eu, difficulty in preparing and storing RI sources with finite lifetimes has prevented the wide and familiar use of Mössbauer spectroscopy for other elements. In contrast, energy-tunable, highly bright, well-collimated, pulsed, and polarized SR is very distinct.

In this study, we have developed a new method that yields Mössbauer absorption spectra using SR. This method was proposed in 1974 [2]; however, from a contemporary viewpoint, it is appropriate for synchrotron measurements of Mössbauer nuclides with high-energy and short-lifetime excited levels. We present the first experimental results of the Mössbauer absorption spectra of <sup>73</sup>Ge and <sup>57</sup>Fe using the developed method.

The use of nuclear Bragg scattering in previously developed Mössbauer spectroscopy using SR provides a Mössbauer source with a single-line energy spectrum [3]. However, such a source has been developed only for <sup>57</sup>Fe [3–5], because, in the case of other elements, it is difficult to produce perfect single crystals with pure nuclear reflections. The standard approach adopted using SR is nuclear resonant forward scattering (NFS) measurement in the time domain [6]. This established method is most effective for nuclides with relatively low excited-state energy and a sufficiently long lifetime. Si avalanche photodiode (APD) detectors are mostly used in NFS measurements [7]. The efficiency in the detection of high-energy x rays increases when a thick Si layer is used; however, the time resolution

decreases. Despite the drawback, it was recently shown that NFS is applicable to the high-energy nuclide <sup>61</sup>Ni (67.41 keV) using multielement (stacked) APDs [8]. A nuclear lighthouse effect is effective for high-energy short-lifetime excited states [9]; however, the sample environment in such a case is severely restricted. A heterodyne (stroboscopic) detection method for NFS [10,11] measurements is effective for nuclides with a very long lifetime; however, the application of this method to high-energy excited states may be difficult, as discussed above.

The concept of the proposed method is similar to that of conventional (conversion electron) Mössbauer spectroscopy and heterodyne detection method using SR [10]. In addition to deexcited  $\gamma$  rays, in this method, fluorescent x rays and internal conversion electrons, which are easier to detect than high-energy  $\gamma$  rays using an APD detector, are measured only as a function of the Doppler velocity. In this method, two targets—a transmitter and a scatterer—containing the same resonant Mössbauer nuclides are used; the scatterer is placed behind the transmitter on the path of the synchrotron beam. The transmitter or scatterer is Doppler shifted using a common Mössbauer velocity transducer, and delayed  $4\pi$  scattering from the scatterer is measured as a function of the relative velocity using a detector placed below and/or above the scatterer. The experimental setup for <sup>73</sup>Ge measurement is shown in Fig. 1. This velocity-dependent scattering intensity yields a spectrum in the energy domain. When the resonance energy of the scatterer is considerably different from that of the transmitter, radiation at the resonance energy of the scatter is attenuated when the  $\gamma$  rays pass through the transmitter due to electronic processes and nuclear resonant inelastic absorption; the attenuation rate is almost independent of the relative energy when this energy is large. In addition to the attenuation, strong nuclear resonance absorption occurs in the transmitter when the relative energy is zero or small. Therefore, if we measure the

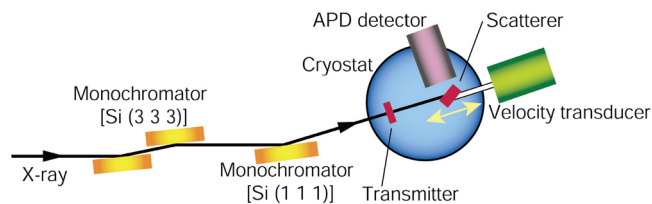


FIG. 1 (color online). Schematic drawing of experimental setup. A double-crystal Si(333) premonochromator was used to handle the high heat load of undulator radiation, and 68.752 keV radiation was obtained using a Si(111) monochromator, which removes the undesirable first harmonic radiation. The transmitter and scatterer were cooled in a cryostat, and the scatterer was moved in the triangle mode using a velocity transducer. The glancing angle of the incident radiation with respect to the surface of the scatterer is approximately  $5^\circ$ , and delayed emission from the irradiated surface of the scatterer was measured using a multielement Si-APD detector ( $4 \times 2$  APDs, each with a detection area of  $3 \times 5$  mm<sup>2</sup>).

scattering from the scatterer as a function of the relative energy (velocity), a local minimum is observed when the energy is zero. This energy spectrum corresponds to a Mössbauer spectrum.

The 68.752 keV third excited state of  $^{73}\text{Ge}$  [12] has suitable features (linewidth and internal conversion coefficient) to be observed, although this state is only weakly populated by the decay of  $^{73}\text{Ga}$  and its observation using an RI source is difficult. Therefore, in previous Mössbauer experiments, the direct population of this level was achieved by an in-beam Coulomb excitation method [13].

Prior to the measurement of  $^{73}\text{Ge}$ , the  $^{57}\text{Fe}$  Mössbauer effect was measured by using a well-known sample of  $\alpha\text{-Fe}_2\text{O}_3$  to confirm the validity of our method and concept. A powder sample of  $\alpha\text{-Fe}_2\text{O}_3$  (not enriched,  $^{57}\text{Fe}$ : 2 mg/cm<sup>2</sup>) was used as a transmitter, and a Pd metal foil (thickness: 25  $\mu\text{m}$ ) containing  $^{57}\text{Fe}$  (2%) was used as a scatterer. The measurement was performed at 298 K at the Japan Atomic Energy Agency (JAEA) beam line (BL11XU) of SPring-8. The storage ring was operated in a special timing mode (1/7 filling + 5 bunches), and only four of the five single bunches were used for observing the Mössbauer spectrum. The delayed scattered signals within a time window from 6 to 650 ns were counted ( $\sim 40$  counts/s) after each prompt pulse, and the total acquisition time was about 7 h. The measured Mössbauer spectrum is shown in Fig. 2. A hyperfine split sextet is clearly observed, and the positions of the peaks in the spectrum were in agreement with those previously observed using an RI source within the experimental errors (0.05 mm/s) [14]. This result confirms that our developed system functions effectively and that the proposed method is applicable for Mössbauer measurements.

We performed  $^{73}\text{Ge}$  measurements at the nuclear resonant scattering beam line (BL09XU) of SPring-8. To confirm the possibility of carrying out Mössbauer measurements of a sample made from natural Ge ( $^{73}\text{Ge}$ :

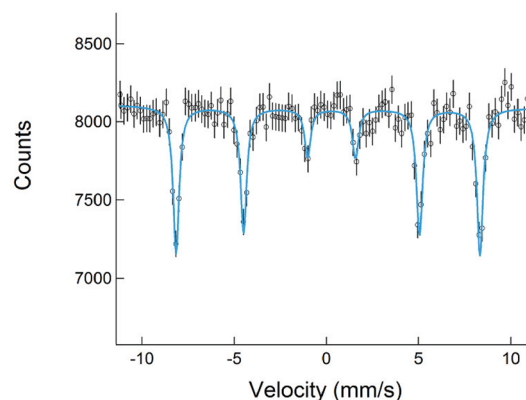


FIG. 2 (color online). Mössbauer spectrum of  $^{57}\text{Fe}$  observed at 298 K using SR. A powder sample of  $\alpha\text{-Fe}_2\text{O}_3$  was used as the transmitter, and a Pd metal foil containing  $^{57}\text{Fe}$  (2%) was used as the scatterer. The solid line shows the fitted spectrum with Lorentz line shapes.

7.73%), we used a powder sample of  $\text{Li}_2\text{GeO}_3$  (not enriched,  $^{73}\text{Ge}$ : 9.4 mg/cm<sup>2</sup>) as the transmitter (20 K). A disk (diameter: 10 mm) of enriched  $\text{GeO}_2$  powder (12 mg, 96.4%  $^{73}\text{Ge}$  enriched, rutile structure with a tetragonal unit cell) was used as the scatterer (77 K). The storage ring was operated in a 203-bunch mode, yielding a bunch distance of 23.6 ns. First, the time spectrum of  $\text{GeO}_2$  was measured to confirm the resonance excitation of the third excited state. This state mainly decays directly to the ground state; however, a small fraction of this state decays to the first excited state. To remove the small contribution of emission from the first excited state (13.2845 keV [12]), a 3 mm thick Al plate was placed at the entrance of the APD detector. This Al plate was removed at the time of the Mössbauer spectrum measurement. The measured time spectra are shown in Fig. 3. The lifetime obtained by fitting is 2.42 (10) ns and is consistent with the reported value [12]. Next, the  $^{73}\text{Ge}$  Mössbauer absorption spectrum was measured; it is shown in Fig. 4. In this case, fluorescent

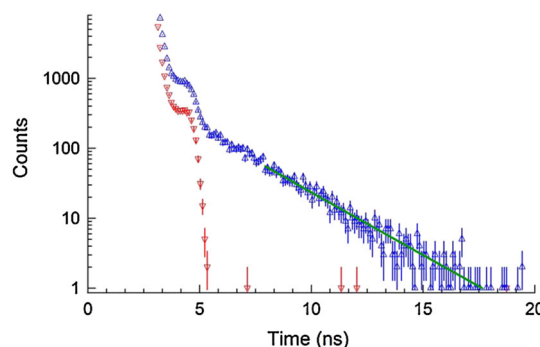


FIG. 3 (color online). Time distribution of nuclear resonance scattering of SR by  $^{73}\text{Ge}$  in  $\text{GeO}_2$ . The upward and downward triangles show measurement results obtained under resonance and off-resonance conditions, respectively. The measured resonance spectrum was fitted with an exponential function in the time interval of 8–19 ns in order to avoid the strong influence of prompt pulses.

x rays were mainly detected following deexcitation, with 68.752 keV  $\gamma$  rays making a small contribution. The delayed scattering with a time window from 6 to 19 ns after each prompt pulse was counted ( $\sim 150$  counts/s). The total acquisition time was about 90 h. The theory about spatially incoherent ( $4\pi$ ) nuclear resonant scattering has already been developed by Smirnov *et al.* [15,16]. This theory can be applied to the description of the obtained absorption spectrum by explicitly adopting the difference between the resonance energies of the transmitter and scatterer, caused by Doppler motion and hyperfine interactions (isomer shift, etc.). Note that each Ge ion in  $\text{GeO}_2$  (tetragonal structure,  $P4_2/mnm$ ) is surrounded by six oxygen ions in a slightly distorted octahedral configuration; however, no quadrupole splitting has been reported [13]. Furthermore, in  $\text{Li}_2\text{GeO}_3$  (orthorhombic,  $\text{Cmc}2_1$ ), each Ge ion is coordinated by four oxygen ions, forming a  $\text{GeO}_4$  tetrahedron. This local structure is similar to that in  $\text{GeO}_2$  (trigonal quartz structure,  $P3_221$ ), whose  $^{73}\text{Ge}$  Mössbauer spectrum showed no conclusive evidence for quadrupole splitting [13]. Furthermore,  $\text{Li}_2\text{GeO}_3$  and  $\text{GeO}_2$  are non-magnetic. Therefore, we assumed no hyperfine splitting for Ge atoms in  $\text{GeO}_2$  and  $\text{Li}_2\text{GeO}_3$ . In this case, propagating coherent field amplitudes of the transmitter,  $E_t(w)$ , at a dimensionless frequency  $w$  of the incident x ray in the unit of the natural width of the nuclear excited state and propagating coherent field amplitudes of the scatterer,  $E_s(w, w_s, z)$  at  $w$ , relative shift  $w_s$ , and depth  $z$  of the scatterer are given by the following expressions:

$$E_t(w) = E_{0t} \exp\left(-\frac{\mu_{et} z_t}{2}\right) \exp\left(-i \frac{\mu_{nt} z_t}{2(2w + i)}\right),$$

$$E_s(w, w_s, z) = E_{0s} \exp\left(-\frac{\mu_{es} z}{2}\right) \exp\left(-i \frac{\mu_{ns} z}{2(2(w - w_s) + i)}\right),$$

$$I_A(w_s) = C_A \int_{\tau_1}^{\tau_2} d\tau \int_0^{z_s} dz \left| \int \frac{dw}{2\pi} \frac{\exp(-iw\tau)}{w - w_s + i/2} E_t(w) E_s(w, w_s, z) \right|^2,$$

$$I_C(w_s) = C_C \int_{\tau_1}^{\tau_2} d\tau \int_0^{z_s} dz \left| \int \frac{dw}{2\pi} \exp(-iw\tau) (E_t(w) E_s(w, w_s, z) - 1) \right|^2, \quad I(w_s) = I_A(w_s) + I_C(w_s) + I_B,$$

where  $z_s$  is the thickness of the scatterer;  $I_A$ ,  $I_C$ , and  $I_B$  are the intensities corresponding to the above-mentioned three processes;  $C_A$  and  $C_C$  are constants; and  $\tau_1$  and  $\tau_2$  are the starting and ending times, respectively, of the measured time window in units of the lifetime of the nuclear excited state. By thin-sample approximation, a Lorentzian line shape can be obtained in the time range ( $\tau_1 = 0$ ,  $\tau_2 = \infty$ ) by ignoring the contribution of  $I_C$  [16]. The isomer shift of  $\text{Li}_2\text{GeO}_3$  relative to tetragonal  $\text{GeO}_2$ , obtained by fitting the calculated spectrum to the observed spectrum, is  $-0.21(12)$  mm/s. The observed linewidth of the spectrum is broader (4.4 mm/s) than that expected for ideally thin samples (2.2 mm/s), and this broadening is due to the use of relatively thick samples. The features seen at the wing are thought to be a result of statistical errors.

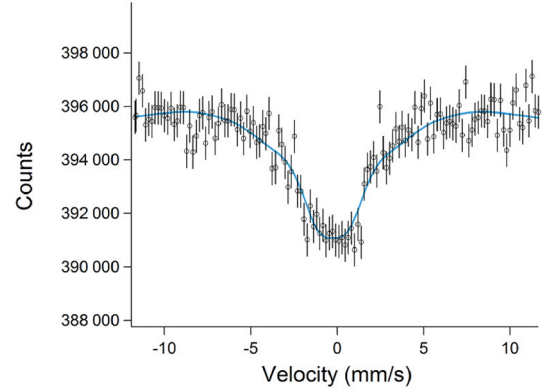


FIG. 4 (color online). Mössbauer spectrum of  $^{73}\text{Ge}$  measured using SR. A powder sample of  $\text{Li}_2\text{GeO}_3$  was used as the transmitter, and a powder sample of  $\text{GeO}_2$  was used as the scatterer. The solid line shows the fitted spectrum described in the text.

where  $z_t$  denotes the thickness of the transmitter;  $\mu_{nt}$  ( $\mu_{ns}$ ), the linear absorption coefficient of radiation by the nuclei at resonance in the transmitter (scatterer);  $\mu_{et}$  ( $\mu_{es}$ ), the electronic absorption coefficient of the transmitter (scatterer); and  $E_{0t}$  ( $E_{0s}$ ), the amplitude of the radiation field at the entrance of the transmitter (scatterer). Under the measurement conditions employed in our study, the following two processes are dependent on the relative shift  $w_s$ : nuclear recoilless absorption of radiation ( $A$  channel in Ref [15]) and scattering of the radiation due to photoelectron absorption ( $C$  channel in Ref. [15]). The dependence of other processes such as nuclear absorption of radiation with recoil ( $B$  channel in Ref. [15]) on the relative shift is small and thus ignored. The absorption spectrum intensity  $I(w)$  can be expressed as follows:

In this method, both the transmitter and the scatterer should have finite recoilless fractions. However, finding only one single-line good reference material enables us to carry out the measurements of the samples with low recoilless fractions. It is desired that the scatterer consists of only resonant nuclides or light elements except the resonant nuclides; the enrichment of the scatterer is useful for reducing the unwanted photoelectron absorption of the nuclear resonant forward scattering, which reduces the relative depth of the resonant absorption in the measured spectrum. Furthermore, a thin rectangular-flat plate sample or a film is favorable as a scatterer, and it should be placed slightly inclined from the direction of the incident beam to be illuminated thoroughly for obtaining a good quality spectrum.



TABLE I. Comparison between SR-based Mössbauer spectroscopy and Mössbauer spectroscopy using radioactive sources.

	Synchrotron radiation [proposed energy domain method (E) and time domain NFS method (T)]	Radioactive sources
Surface, interfaces, multilayers	Clean, unclean, and nanostructured samples (E); limited to clean surfaces (T)	Clean, unclean, and nanostructured samples
Multiple extreme conditions <sup>a</sup> , imaging	Relatively easy, sub- $\mu\text{m}$ resolution is possible (E,T)	Usually not easy, limited to $\mu\text{m}$ resolution
Applicable isotopes	Short- and extremely long- lived and high-energy isomers are possible (E); efficient for low-energy and sufficiently long-lived isomers (T)	Isotopes for which appropriate sources are available

<sup>a</sup>High pressure ( $\sim 200$  GPa), applied magnetic field ( $\sim 10$  T), high ( $\sim 1000$  K) or low ( $\sim$  mK) temperature.

To prevent the time response of the APD detector from being affected by strong prompt incident radiation pulses, the measurement was performed from 6 ns after each prompt pulse, and this relatively late start time of measurement reduced the measured delayed counts. Since the energy width of the incident synchrotron radiation ( $\sim \text{eV}$ ) is considerably wider than that of the energy range usually used in Mössbauer spectroscopy ( $< 100 \mu\text{eV}$ ), almost all of the incident radiation is unnecessary. Therefore, by using a high- [17] or medium- [8] resolution monochromator, which reduces unnecessary incident radiation and allows the use of an earlier start time for the measurements, an increase in the delayed counts is expected. In particular, the use of the high-resolution monochromator, which reduces the contribution of phonons, will give a high-quality spectrum because scattering with phonons from the scatterer increases the unwanted background. Since we used the natural sample as the transmitter to demonstrate the possibility of measurement of a natural sample, the measurement took considerable amount of time. However, the use of an enriched sample as a transmitter, an optimized thin rectangular-flat plate as a scatterer, a large-area detector, and even a medium-resolution monochromator reduce the acquisition time by more than 1 order of magnitude.

It should be noted that exact line shapes of the Mössbauer spectra are obtained by the transmission integral method [18]; the exact line shape of our spectrum is obtained by the above-mentioned method. This indicates another aspect of the proposed method that it is similar to delayed coincidence Mössbauer spectroscopy [19,20] and it yields a narrow and modified line shape. In fact, the changes in the line shape have been previously observed using SR by different measurement methods [11,21].

As a benefit of the excellent features of SR, the applicability of SR-based Mössbauer spectroscopy will increase. The comparison between SR-based Mössbauer spectroscopy and Mössbauer spectroscopy using radioactive sources is shown in Table I.

In conclusion, in this study, the Mössbauer spectrum of  $^{73}\text{Ge}$  was successfully measured using SR for the first time,

and the validity of the proposed method was confirmed. The freedom in selecting the scatterer or transmitter as a sample reduces the restrictions on type of samples and sample environments. With the wide availability of Mössbauer nuclides, this method enables advanced measurements in various scientific fields such as microscopic measurements, measurements of ultrasmall samples under extreme conditions, and measurements of complex nanostructured materials.

We are thankful to the entire staff of SPring-8 for their support. This study was conducted under the Power User Priority Program of SPring-8.

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